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Measuring the Spatial Variability of Ammonia Emission From Feedlot Surfaces as Identified by Electromagnetic Induction Methods

B.L. Woodbury, Agricultural Engineer

USDA-ARS U.S. Meat Animal Research Center, P.O. Box 166, Clay Center, Nebraska
woodbury@email.marc.usda.gov

D.N. Miller, Microbiologist

USDA-ARS U.S. Meat Animal Research Center, P.O. Box 166, Clay Center, Nebraska

R.A. Eigenberg

USDA-ARS U.S. Meat Animal Research Center, P.O. Box 166, Clay Center, Nebraska

J.A. Nienaber

USDA-ARS U.S. Meat Animal Research Center, P.O. Box 166, Clay Center, Nebraska

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Abstract. *Understanding the interactions between the environment and emission from livestock waste is essential in developing management practices designed to minimize negative environmental consequences. However, the protocol and equipment necessary to investigate these interactions at the laboratory or field-scale do not exist or are expensive. Therefore, an inexpensive dynamic flux*

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chamber (cost: <\$400 per unit) was developed to measure gaseous emissions from cattle manure in laboratory and field experiments. The hemispherical stainless steel chamber was constructed with an internal gas mixing fan. A port was attached to the chamber top, which facilitated the collection of headspace gas samples for greenhouse gases and volatile organic compounds (VOC) by solid phase microextraction (SPME). The chamber was tested to evaluate flow characteristics, and was found to perform very similarly to a continuous flow stirred reactor. Thus, concentrations measured at the sampling port were indicative of concentrations anywhere in the headspace. Preliminary results indicate a general gradation of ammonia loss from the feed bunk apron to the down-gradient end of the pen when chamber data was co-krigged with ratio electromagnetic induction (EMI) data, that was cropped to eliminate influence of metal fence. The greatest losses were measured just down-gradient from the feed bunk apron. This is most likely a result of the time the animal spends at or near the feed bunk and the amount of urine that is deposited on the bunk apron. This urine runs off and accumulates in the soil near the apron, resulting in high ammonia volatilization. Additional studies are planned to refine EMI mapping and chamber sampling techniques to minimize statistical uncertainties. However, preliminary results indicate that using EMI may be useful in better understanding ammonia emission spatial variability.

Keywords. *Dynamic flux chamber, Ammonia emissions, Electromagnetic induction*

Introduction

Many different gases, such as NH_3 , greenhouse gases, and VOC, associated with malodor (volatile fatty acids, aromatics, sulfides amides, and alcohols) are emitted from beef cattle waste deposited on feedlot surfaces (Hutchinson et al., 1982; Baek et al., 2003; Duysen et al., 2003; Gay et al., 2003; McGinn et al., 2003; Koelsch et al., 2004). Ammonia emissions from beef feedlots have received much attention because of the potential threat to the environment. As such, considerable efforts have been spent refining measurements of ammonia from feedlot surfaces. Regrettably, these measurements are primarily collected using equipment that is expensive or labor intensive. Furthermore, considerable expertise and operator input is needed to position and collect multiple measurements to account for extensive spatial variability.

Research has been initiated to understand the spatial variability of nitrogen deposition on feedlot surfaces and manage these surfaces to reduce losses (Berry and Miller, 2005; Miller and Berry, 2005; Woodbury et al., 2001). Additional research combining electromagnetic induction (EMI), GPS, and geostatistical imaging techniques shows great potential for mapping the spatial distribution of manure within feedlot pens (Eigenberg et al., 2002; Eigenberg et al., 2003). As a result, interest has grown in utilizing EMI mapping techniques for evaluating ammonia emission spatial variability from feedlot soils. Unfortunately, robust techniques and inexpensive, versatile equipment needed to verify EMI images at the field-scale do not exist or are prohibitively expensive. Therefore, the objectives of this study were to 1) design a low-cost dynamic flux chamber, 2) evaluate this chamber's flow characteristics and suitability for field studies, and 3) combine chamber data from field studies with electromagnetic induction methods to describe the special variability of ammonia emissions from feedlot surfaces.

MATERIALS AND METHODS

Dynamic Flux Chamber Design

A parts list and vendors used for construction of the head-space chamber system is listed in Table 1. A semi-hemispherical stainless steel (SS) vessel (7.6 L) was used as the dynamic flux chamber (Fig. 1A). A port was fixed at the chamber top using a 6.5 mm national pipe thread (NPT) SS bulkhead fitting. The bulkhead fitting was sealed with an O-ring, and the stem protruded into the chamber headspace approximately 25 mm. The external connector was attached to a 6.5 mm NPT SS tee. One end of the tee was fitted with septa to allow insertion of a SPME portable field sampler (Supelco, Bellefonte, PA) for collection of VOC or a syringe needle for collecting permanent gases, such as O_2 , CO_2 , CH_4 , and N_2O (Fig. 1B). The assembly was oriented such that a SPME fiber would pass through the tee toward the chamber to minimize breakage during insertion. The second connector of the tee was fitted with a 6.5 mm hose barb fitting (Fig. 1B). This hose barb was attached to a 0.25 m long, 6.5 mm diameter polyvinyl chloride (PVC) tube, which was connected to a midget bubbler (Fig. 1C). This bubbler was contained inside a 23 × 85 mm glass vial filled with 12 ml of a 10 mM H_3PO_4 ammonia trap solution (Fig. 1C). The vacuum side of the bubbler was connected

to the inlet port of a battery operated air pump. A nylon membrane syringe filter with a 0.45 μm pore diameter was placed in-line to limit inadvertent pump contamination with acid trap solution (Fig. 1D). The pump (Fig. 1E) discharge port was connected to two 6.5 mm diameter compression fitting tees using two 0.25 m long, 6.5 mm diameter, rigid wall vinyl tubing. Four 0.10 m long, 6.5 mm diameter, rigid wall vinyl tubes distributed discharge to four 6.5 mm compression fitting 90° elbow bulk head fittings. These fittings segmented the circular chamber into quadrants (Fig. 1F). Elbow fittings were placed such that air inlet was approximately 50 mm above the feedlot/sample surface (Fig. 1F). Inside the headspace of the chamber was a 40 mm, 12 volt axial flow fan moving approximately 130 L min⁻¹ (Fig. 1G). The fan was suspended in the center of the headspace approximately 70 mm above the feedlot/sample surface. Fan air-flow direction was from surface up to the chamber top. Fan power was supplied through a 12V bulk head connector located at the chamber top (Fig. 1H).

Methane Tracer Studies

Four tracer studies were conducted to test dynamic flux chamber physical properties. The chamber was placed on a flat plate so that the total headspace volume tested was 7.6 L. Flow rates through the exit port were set at 1.18, 1.15, 1.14, and 1.14 L/min, respectively. A methane pulse of 50 cm³ was injected through an inlet port. Total injected methane mass was adjusted for atmospheric pressure at the time of the test. Several air samples were taken by syringe through the chamber septa port. Sampling intervals were variable (0 to 40 min) with short intervals at the beginning, and longer intervals at the end of the tracer study. Total sampling time was six dilutions or more. Several initial samples were taken before the pulse injection to establish background methane concentrations. Methane concentrations were determined relative to standard mixes (Scotty Specialty Gases, Plumsteadville, PA), using an 8610C gas chromatograph (SRI Instruments, Torrance, CA) equipped with helium ionization and thermal conductivity detectors as previously described (Miller and Berry, 2005).

Field Application

Five chambers were constructed and tested on an experimental cattle feedlot at the USDA-ARS U.S. Meat Animal Research Center in south-central Nebraska. Chambers were placed in a 30 m X 90 m feedlot pen (pen width was east-west, length was north-south), along three transects starting down-slope from the feed bunk apron. Slope was south to north, with the bank at the southern end of the pen. Transects were placed perpendicular to the bunk at 7.5, 15, and 22.5 m from the west edge of the pen (Fig. 3). Six points along each transect were measured starting a 1.5 m down-slope from the bunk apron and at intervals of 15 m thereafter. Two additional points were measured at the northern edge of the pen's central mound. Chambers were operated in recirculation flow mode (1 L/min) for 30 minutes in order to trap NH₃. Ammonia was trapped in a solution of 10 mM phosphoric acid. Ammonia content of the liquid in the acid trap was measured, using the indophenol blue method (Miller and Berry, 2005).

RESULTS AND DISCUSSION

Flow Characteristics

Tracer study break-through-curves (BTC) are illustrated in Fig.2. The first sample taken was five seconds after injection. The abrupt rise and subsequent decrease in methane head-space concentration indicates the pulse was evenly distributed during this first interval. Methane concentrations decreased abruptly, and then asymptotically approached background concentrations by 1000 seconds. Cumulative mass percentages of methane collected for each tracer study are illustrated in Fig. 2. Calculated percentages of methane collection were determined by summing the area under methane concentration curve defined by the individual sampling time interval. Calculated cumulative recovery percentages for the tracer studies ranged from 93.0 to 103.8% (Table 2) and averaged 98.8% recovery, which did not differ from the expected 100% recovery ($P = 0.65$). Percent recovery, however, was very dependant on the ability to precisely measure the initial pulse mass entering the chamber, and likely explains the variation observed between tests.

Measured break-through-curves typified an ideal continuous flow stirred reactor (CFSR). Generally, an ideal CFSR would have concentrations of 37 and 5%, respectively, of the theoretical initial chamber concentration (assuming standard conditions) at one and three dilutions. These tracer studies yielded average concentrations of 37.5 and 5.5% of original concentration at one and three dilutions, respectively (Fig. 2). Deviation from the ideal reactor may be explained by injection of the tracer in only one inlet port, and not at the chamber center. During the initial five second mixing time, some of the tracer may have preferentially been removed from the chamber affecting peak concentrations and recovery. However, this process appears to be negligible. Using physical measurements of dynamic flux chamber and pulse test data, values were determined for RT_C and RT_E (Table 2). Although RT_C values were slightly higher on average, a two-sample paired t-test demonstrated that RT_C did not differ from RT_E ($P = 0.38$).

It is widely accepted that emission values measured using covered chambers, similar to the dynamic flux chamber described here, are not the best measures of actual system emissions. Actual emissions are more confidently measured using wind tunnel or other non-invasive techniques such as micrometeorology (Harper et al., 1999; Meisinger et al., 2001; Arogo et al., 2003). Some of the potential drawbacks with using covered chambers include the small sample surface area relative to the pen surface spatial heterogeneity, and modified gas exchange between the surface and atmosphere due to the restricted air flow imposed by the chamber. However, the application of flux chambers proves very useful for evaluating relative emission differences in controlled environments, and their continued usefulness as a field survey instrument is evident (for a recent example, see DeSutter and Ham, 2005).

Field Application

Dynamic flux chambers were placed on grid sampling points in a feedlot pen, and ammonia samples were collected for approximately 30 minutes. Ammonia

concentrations (μM) at each sampling point are listed in Fig. 3. Concentrations were not converted to flux rates because only relative differences were of interest. Highest ammonia concentrations were found near the feed bunk apron.

Ammonia concentrations were krigged and co-krigged with horizontal (PRP dipole), ratio (PRP/HCP dipole) orientation, and ratio with pen edges cropped to remove influence of the metal fencing by using ArcGIS (ESRI Software, Redlands, California) geostatistical software. An EMI ratio is a technique that is used to identify near-surface areas that are highly conductive. Root mean squared (RMS) predicted error for each geostatistical analysis is presented in Table 3. The RMS predicted error for the ammonia krig data was 8.72 (Table 3). Ammonia concentrations were co-krigged with PRP dipole and ratio EMI (PRP/HCP dipole orientation) with pen fencing effects, but did not improve RMS predicted error with 8.78 and 8.76, respectively (Table 3). However, co-krigging ammonia data with ratio (PRP/HCP dipole orientation) EMI data, with pen fencing effects removed, did improve RMS predicted error with a value of 8.64 (Table 3). These data are presented graphically in Fig. 4.

Co-krigged ratio data, with pen fencing effects removed, indicates a gradation of ammonia losses. The highest losses are near the feed bunk apron and gradually decreasing as distance from the bunk apron increases. This is most likely a result of the time the animal spends at or near the feed bunk, and the amount of urine that is deposited on the bunk apron. Since the apron is constructed of concrete, the urine runs off and accumulates in the soil near the apron. As a result, the highest ammonia losses would be expected at or near the feed bunk apron.

CONCLUSIONS

An inexpensive (< \$400), portable dynamic flux chamber was developed for use in laboratory and field studies for measuring relative fluxes of a variety of cattle feedlot emissions. The hemispherical stainless steel chamber was constructed with an internal gas mixing fan. A port was fixed at the top of the chamber that could accommodate SPME gas samplers and headspace gas sampling for greenhouse gases. Furthermore, an in-line bubbler was attached for trapping and sampling ammonia. The chamber was tested to determine flow characteristics, and performed as an ideal continuous flow stirred reactor with near 100% recovery of methane tracer, with no difference between the RT_C and RT_E . As a result, concentrations measured at the sampling port are indicative of concentrations anywhere in the headspace. Therefore, the chamber flow characteristics indicate it to be suitable for collection of relative flux rates, but actual flux rates may not be readily determined due to design limitation.

Preliminary results using chamber data co-krigged with ratio EMI, with edges cropped to eliminate metal fencing influences, indicate a general gradation of ammonia loss from the feed bunk apron to the down-gradient end of the pen. The greatest losses were measured just down-gradient from the feed bunk apron. This is most likely a result of the time the animal spends at or near the feed bunk, and the amount of urine that is deposited on the bunk apron. This urine runs off and accumulates in the soil near the apron, resulting in high ammonia volatilization. Additional studies are planned to refine EMI mapping and chamber sampling techniques to minimize statistical uncertainties.

However preliminary results indicate that using EMI may be useful in better understanding ammonia emission spatial variability.

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Table 1. Parts list and vendors for dynamic flux chamber.

Item	Manufacturer	Part /Number	Amount	Total Cost (\$)
SS Chamber	Walmart		1	5.00
Air Pump	SKC Inc.	222-2301	1	130.00
Midget Bubble	Supelco	64834-U	1	50.00
12V Battery	Batteries.com	272388	1	25.00
Circulating fan	Newark	91F7443	1	10.00
Bulk-head elbows	Parker Instru.	4-4C5BZ-SS	4	60.00
Union tee	Parker Instru.	4-4-4JBZ-SS	3	45.00
Hose to pipe adpt.	Parker Instru.	4-4B2HF-SS	1	5.00
Bulk-head male	Parker Instru.	4-4FH2B2-SS	1	10.00
Male connector	Parker Instru.	4-4FBZ-SS	1	7.00
1/4 SS tee			1	3.00
Misc. Elec. connectors	Newark			15.00
Misc. tubes				15.00
			Totals	\$380.00

Table 2. Calculated (RT_C) and experimentally (RT_E) determined retention times and pulse recovery percentages for each tracer test.

Measured Flow $L\ min^{-1}$	RT_C * seconds	RT_E seconds	Pulse Recovery %
1.18	386	390	96.4
1.15	396	395	93.0
1.14	400	394	103.8
1.14	400	392	101.8

* RT_C = Chamber volume (7.6 L)/measured flow \times 60 sec/min

Table 3. Root mean squared error predicted error of geostatistical process.

Statistic	Krig	Co-krig w/PRP	Co-krig w/RPH*	Co-krig w/ RPH Pen edges cropped**
RMS Predicted Error	8.72	8.78	8.76	8.64

* RPH = PRP/HCP (horizontal to vertical dipole orientation)

** Pen edges were cropped because of the influence of the metal fencing of the pen

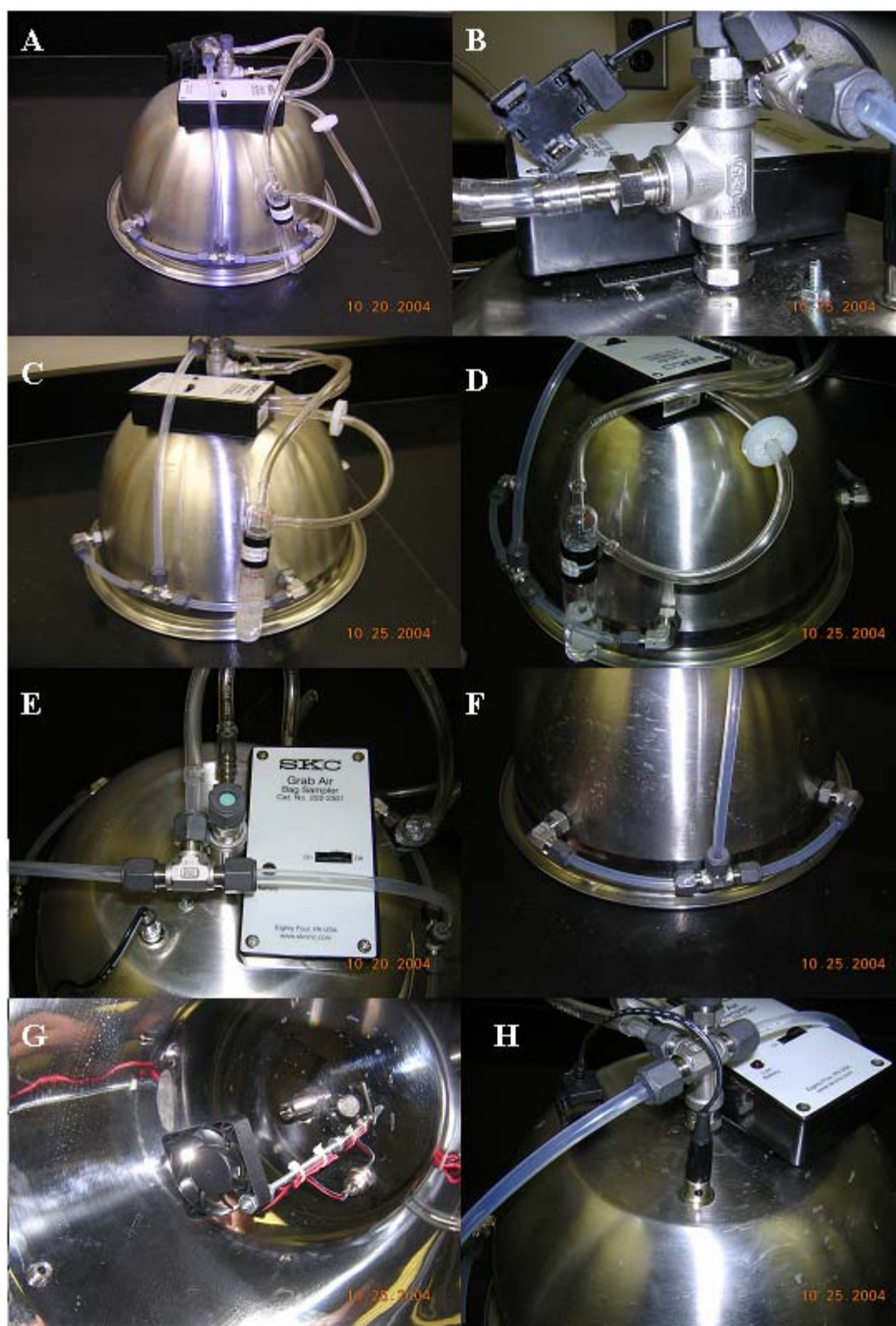


Figure 1. Hemispherical flux chamber set-up for ammonia analysis.

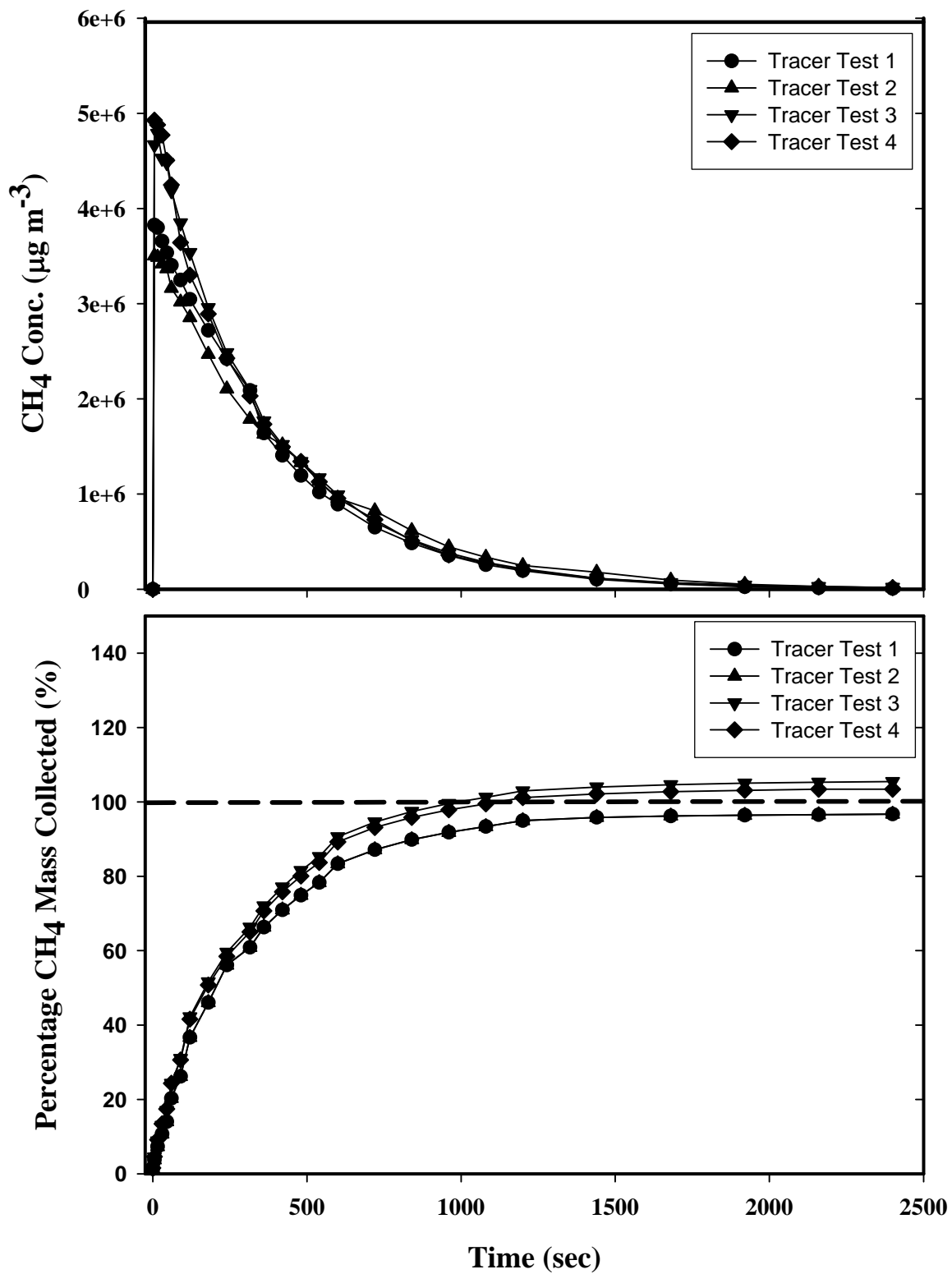


Figure 2. Tracer study break-through-curve and cumulative mass collected curve.

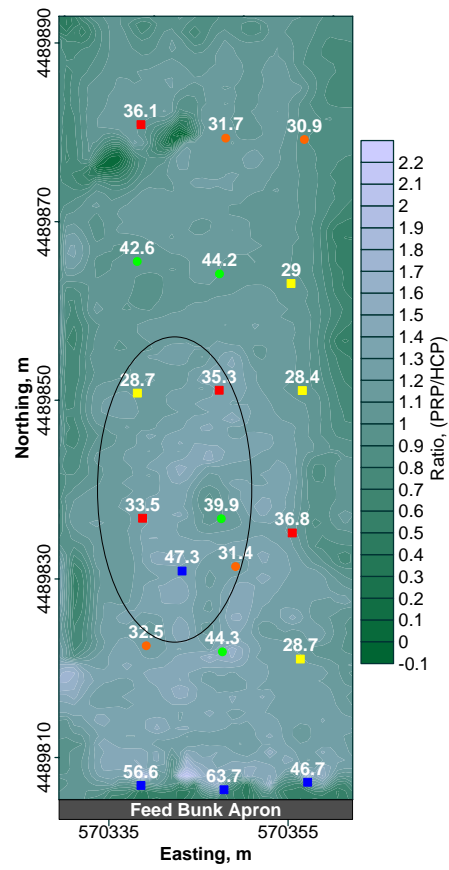


Figure 3. Electromagnetic induction ratio (PRP/HCP dipole orientation) map of the feedlot pen. Points within the pen indicate flux chamber locations and values listed are ammonia concentrations collected in $\mu\text{M L}^{-1}$ for a 30-minute sampling period.

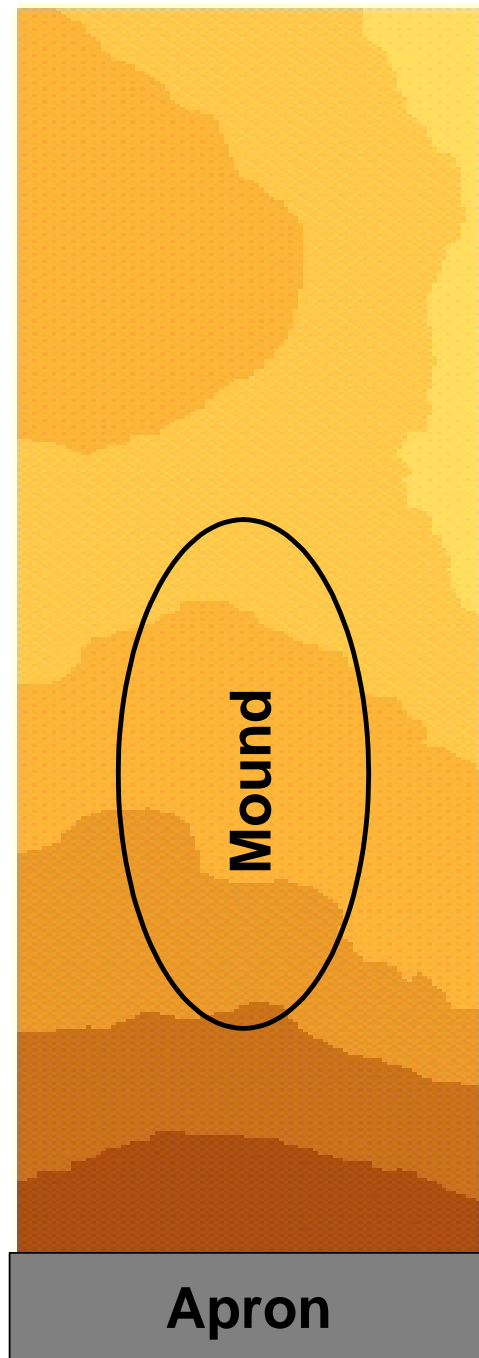


Figure 4. Prediction map indicating the spatially variable ammonia losses resulting from co-krigged ammonia data and ratio electromagnetic induction data with edges cropped. Note the darker regions are areas with higher relative ammonia losses.